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review

OF RECENT
DEVELOPMENTS

D D C Oxidation-Resistant Coatings for Refractory Metals

MAY 21 1969

D. C. Allen • May 2, 1969

COATING DEVELOPMENT FOR COLUMBIUM ALLOYS

Silicide and aluminide coatings for protection of columbium alloys, D-43, Cb-752, C-129Y, XB-88, and Cb-132M, for hundreds of hours to 2500 F are being developed by TRW for application in gas turbine engines and aerospace environments. (1) The coatings were modified with elements such as titanium, chromium, vanadium, and molybdenum. Vanadium was deposited by an activated vacuum-pack process, while molybdenum was deposited by chemical-vapor deposition from MoCl_5 . The Ti-Al and Ti-Al-Si systems were promising for low-temperature applications, giving over 500 hours protection at 1600 F. Of the many combinations investigated, as listed in Table 1, the V-CrTi-Si system was most promising and was extensively investigated. The system showed a superiority over the CrTi-Si system, exhibiting a potential for 1000-hour protection at 1600 to 2200 F and over 200 hours at 2400 F in cyclic oxidation. In oxidation-erosion tests, the V-CrTi-Si system protected substrates up to 200 hours at 2200 F and 100 hours at 2400 F. In oxidation-erosion, ballistic impact, and slow-thermal-cycle tests, both systems were comparable. Although lifetimes to initiation of coating failure were similar in many tests, propagation and growth of oxidation sites were notably slower in the vanadium-modified coating. Such behavior suggests that a self-healing tendency is the principal advantage of the V-CrTi-Si over the CrTi-Si system.

The British have developed a $\text{CbSi}_2\text{-1Fe-1Cr}$ + glaze coating for protection of columbium alloys such as F-48 and SU-16 ($\text{Cb-11W-3Hf-2Mo-0.08C}$). (2) The modified silicide was applied by pack cementation and the glaze by a slurry-sinter process. The best glaze composition studied was $68.4\text{SiO}_2\text{-19.5 Al}_2\text{O}_3\text{-2.0CaO-0.17MgO-5.0K}_2\text{O-5.0Na}_2\text{O}$; this glaze improved coating performance by filling microcracks present in the silicide. The coating gave about 100 hours cyclic oxidation protection at 2010 to 2370 F, generally under simulated gas-turbine-engine-exhaust products. The oxidation resistance was found to be similar to that of Cr-Ti-Si coatings developed in the United States. Room-temperature tensile and miniature Charpy impact tests showed that the silicide-glaze coating maintained the ductility of the uncoated alloy even after oxidation or creep exposure in air for 100 hours up to 2280 F. The Cr-Ti-Si coating tended to embrittle F-48 columbium impact specimens. The coatings slightly reduced the creep strength of F-48 and SU-16 columbium alloys at 2010 to 2280 F.

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A columbium alloy, designated WC-3015, that develops its own protective coating upon air exposure has been investigated by Wah Chang. (3) The alloying additions are 28 to 30 hafnium, 13 to 16 tungsten, 0 to 4 tantalum, 1 to 2 zirconium, and 0.07 to 0.33 carbon. The hafnium provided the oxidation resistance by forming a 0.03 to 0.04-inch-thick coating after 24 hours at 2400 F. Inward diffusion of oxygen was nominal within the estimated maximum exposure period for candidate applications in gas turbine engines. The other additions impart strength and creep resistance. At 1400 F, the yield and tensile strengths were 80 and 100 ksi, respectively, and the elongation was over 15 percent.

OXIDATION OF COATED COLUMBIUM, MOLYBDENUM, AND TANTALUM ALLOYS

The oxidation behavior of the following four systems has been evaluated in supersonic airstreams by NASA: Durak B and Vought IX silicide coated TZM molybdenum, and Cr-Ti-Si- and Cr-MoSi₂-coated Cb-752 columbium alloy. (4) Cyclic (8 minutes) coating life was measured on blunt-nose models at surface temperatures of 2600 to 3000 F at air-stagnation pressures behind the shock wave of 0.03, 0.1, and 5.5 atm. Except for the Vought coating which gave erratic protection, coating life was under 32 minutes at the two lower pressures and about 1 hour at 5.5 atm. The uncoated alloy controls oxidized catastrophically by liquid-phase formation in less than 30 seconds at 2900 to 4000 F, depending on stagnation pressure.

The oxidation of W-Si-coated Ta-10W has been studied between 1830 and 3090 F at an oxygen partial pressure of 150 torr in helium for times up to 1 hour. (5) The TRW coating was prepared by chemical vapor depositing tungsten and vacuum-pack siliciding. The Solar coating (TNV-13) was applied as a 95W-5Ti slurry, sintered, pack silicided in argon near 1 atm, and impregnated with glass frit. As indicated in Figure 1, oxidation of the TRW coating was logarithmic, with oxidation resistance improving with increasing temperature in the range 1830 to 2730 F. At 3090 F, the coating failed catastrophically. According to Figure 2, oxidation of the TNV-13 coating was parabolic between 1830 and 3090 F. Electron-microprobe analyses suggest that the difference can be ascribed to the titanium content of the Solar coating.

TABLE 1. CYCLIC OXIDATION DATA FOR SILICIDE AND ALUMINIDE COATINGS⁽¹⁾

Coating System	Substrate	Coating Deposit, mg/cm ²								Oxidation Life Until Edge Failure, hours	
		Ti	Mo	V	Cr, Ti	Cr	Ta	Al	Si	1600 F	2400 F
Control Coatings											
CrTi-Si	Cb-752	--	--	--	12.7	--	--	--	14.7	16, >1397	54, 131(a)
CrTi-Si	Cb-752	--	--	--	14.8	--	--	--	12.2	96, 96	218, 266
CrTi-Si	C129Y	--	--	--	15.2	--	--	--	13.5	24, 120	218, 218
CrTi-Si	D-43	--	--	--	16.2	--	--	--	11.1	>1157, >1157	218, 218
Si	Cb-752	--	--	--	--	--	--	--	9.1	64	6, 20
Ti	Cb-752	8.6	--	--	--	--	--	--	--	8	1, 1
Al	Cb-752	--	--	--	--	--	--	5.0	--	36, 20, 20	2, 2
Modified Silicide Coatings											
Ti-Mo-Si	Cb-752	13.2	13.6	--	--	--	--	--	8.3(b)	4, 4(a)	2, 7(c)
Ti-Mo-Si	Cb-752	7.2	2.2	--	--	--	--	--	19.2	24, 24(a)	24, (a) 79
Ti-Mo-CrTi-Si	Cb-752	13.2	13.6	--	14.1(b)	--	--	--	10.0(d)	4, 13(a)	1, 54(a)
Ti-Mo-V-Si	Cb-752	13.2	18.0	6.5(d)	--	--	--	--	10.0	4, 8(a)	1, 2(a)
Ti-Mo-V-Cr-Si	Cb-752	13.2	18.0	6.5(d)	--	33.3(d)	--	--	54.0(d)	4, 32(a)	4(a)
Ti-Mo-Cr-Si	Cb-752	13.2	18.0	--	--	16.3(d)	--	--	27.6(d)	4, 4	11, 2(a)
Ti-V-Cr-Si	Cb-752	13.2	--	-3.8(e)	--	34.4	--	--	32.5	8, 4	5, 8(a)
Ti-V-Si	Cb-752	13.2	--	-3.8(e)	--	--	--	--	7.2	24, 28	6, 8
Ti-Ta-Si	Cb-752	13.2	--	--	--	--	-6.0(e)	--	5.1(b)	76	6
Ti-Ta-Si	Cb-752	14.1	--	--	--	--	-5.4(e)	--	5.5(b)	564, 1337	9, 16
Mo-Ti-Si	Cb-752	8.8	15.1	--	--	--	--	--	14.4(b)	8, 32(a)	6, 4(a)
Mo-Ti-Si	Cb-752	6.6	10	--	--	--	--	--	17.6	24, 48(a)	72, 72(c)
Mo-CrTi-Si	Cb-752	--	15.1	--	11.1	--	--	--	7.8	16, 452	374, 379
Mo-V-Ti-Si	Cb-752	14.5	13.9	5.6	--	--	--	--	21.6(d)	4, 8	4, 1
Mo-V-CrTi-Si	Cb-752	--	13.9	5.6	16.3	--	--	--	10.4	1465, 1421	209, 355(c)
Mo-V-Si	Cb-752	--	13.9	5.6	--	--	--	--	6.7	20(c)	8, 9, 9
V-CrTi-Si	Cb-752	--	--	6.8	19.1	--	--	--	7.8	1465, 1421	78, (c) 180
V-Ti-Si	Cb-752	14.7	--	6.8	--	--	--	--	14.8(d)	36, 8(a)	2, 1
V-Ti-Si	Cb-752	8.1	--	1.6	--	--	--	--	16.9	600, 840	72, 72(a)
V-Ti-Si	Cb-752	9.7	--	6.1	--	--	--	--	15.1	984, 1032	48, (a) 175
V-Mo-Ti-Si	Cb-752	11.1	26.6(d)	6.8	--	--	--	--	10.8	4, 4(c)	7, 4
V-Mo-CrTi-Si	Cb-752	--	26.6(d)	6.8	16.9(d)	--	--	--	12.2	8, 500	5, 13
V-Cr-Si	Cb-752	--	--	6.8	--	25	--	--	20.3	4, 4(c)	25, 24
Mo-CrTi-Si	Cb-752	--	11	--	17.8	--	--	--	21.3	128, (a) 136	49, 32
V-Al-CrTi-Si	Cb-752	--	--	5.5	19.4	--	--	12.5	17.2	567, 670	787, 636
V-Al-CrTi-Si	Cb-752	--	--	1.4	11.2	--	--	10.5	16.5	144, 567	286, 334
Modified Aluminide Coatings											
Ti-Al	Cb-752	4.6	--	--	--	--	--	5.6	--	20	4, 4
Ti-Al	Cb-752	16.8	--	--	--	--	--	4.4	--	64	3, 3
Ti-Al-Si	Cb-752	4.6	--	--	--	--	--	5.6	4.9	24	9, 15
Ti-Al-Si	Cb-752	16.8	--	--	--	--	--	4.4	13.9(b)	8	3, 8
Al-Ti	Cb-752	7.8	--	--	--	--	--	5.0	--	4, 4	1, 1
Al-Ti-Si	Cb-752	7.8	--	--	--	--	--	10.6	30.0(b)	8	1
Ti-V-Al-Si	Cb-752	13.2	--	-3.8(e)	--	--	--	5.8	2.5(b)	8, 8(c)	2, 2(a)
Ti-Al-Si	Cb-752	13.2	--	--	--	--	--	5.8	3.4(b)	28, 52	50, 146
Ti-Al	Cb-752	13.2	--	--	--	--	--	6.3	--	124, 564	6, 9(a)
Ti-Ta-Al	Cb-752	13.2	--	--	--	--	-5.4(e)	1.9	--	76, 180	12, 12(a)
Ti-Al	D-43	10.6	--	--	--	--	--	3.9	--	24	--
Ti-Al	D-43	21.6	--	--	--	--	--	7.2	--	374	--
Ti-Al	D-43	27.2	--	--	--	--	--	7.2	--	998	--
Ti-Al-Si	D-33	10.6	--	--	--	--	--	1.9	19.6	24	--
Ti-Al-Si	D-43	21.6	--	--	--	--	--	3.9	19.6	247	--
Ti-Al-Si	D-43	27.2	--	--	--	--	--	7.2	19.6	583	--

- (a) Surface failure.
 (b) Rough deposit.
 (c) Both surface and edge failure.
 (d) Spalled.
 (e) Weight loss, no deposition.

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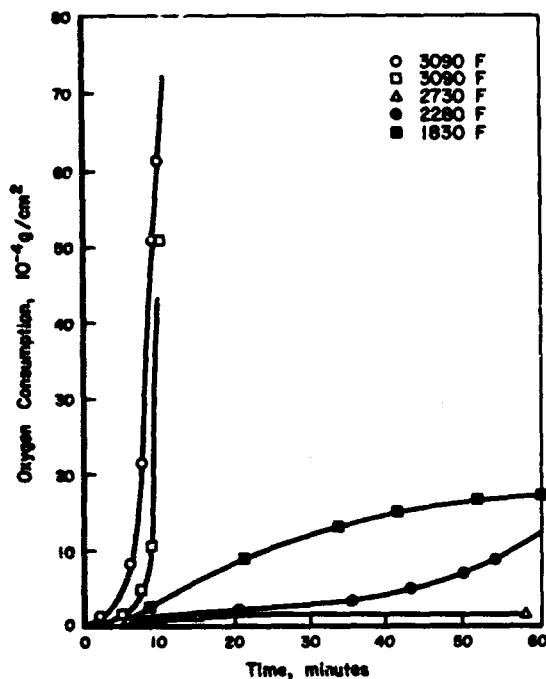


FIGURE 1. OXIDATION OF TRW W-Si-COATED Ta-10W AS A FUNCTION OF TEMPERATURE(5)

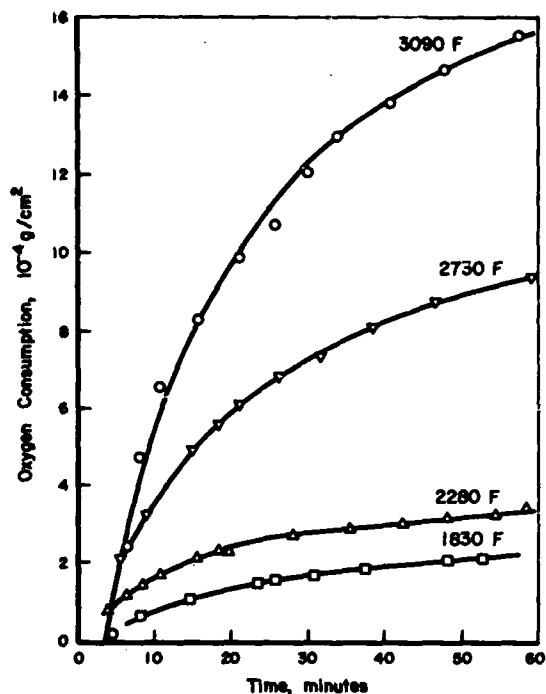


FIGURE 2. OXIDATION OF SOLAR TNV-13-COATED Ta-10W AS A FUNCTION OF TEMPERATURE(5)

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